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EVALUATION OF A SIMPLE MODEL FOR PREDICTING PHOSPHORUS REMOVAL --ETC(U)
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Evaluation of a simple model for predicting phosphorus removal by soils during land treatment of wastewater

J.C. Ryden, J.K. Syers and I.K. Iskandar

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>This report evaluates a simple P balance model to predict site longevity with respect to P removal during land treatment of wastewater. The model is based on measured inputs and outputs of P at the treatment site and on an estimate of the P storage capacity of the soil profile. Sorption of P by three soils used for land treatment conformed to the P sorption model based on a generalized isotherm. Laboratory sorption tests were used to predict P storage capacity of the soil profiles at a solution P concentration equivalent to that in the effluent applied to the soil. For two soil profiles the P balance model predicted site longevity of approximately 50 and 210 years. The existing depth of P enrichment in these profiles predicted from the model agreed closely with measurements of P enrichment based on amounts of NaOH-extractable P and on measured soil solution P concentrations.</p>		

PREFACE

This report was prepared by Dr. J.C. Ryden, Principal Scientific Officer, the Grassland Research Institute, England; Dr. J.K. Syers, Professor and Chairman, Department of Soil Science, Massey University, Palmerston North, New Zealand and Dr. I.K. Iskandar, Research Chemist, Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL).

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EVALUATION OF A SIMPLE MODEL FOR PREDICTING PHOSPHORUS REMOVAL BY SOILS DURING LAND TREATMENT OF WASTEWATER

J.C. Ryden, J.K. Syers and I.K. Iskandar

INTRODUCTION

About 10 or 15 years ago, there was considerable controversy over the relative effect of external P input to lakes versus internal input (release of P from sediment) on the excessive fertilization of water bodies. It has since been established, however, that reducing the external P input to lakes can, in many cases (such as Lake Washington, Seattle), reduce algal growth in proportion to the reduction in the external P load. Reducing P concentration in wastewater to $< 0.1 \mu\text{g P/mL}$ by advanced waste treatment methods was necessary to achieve this reduction in P pollution.

Land application of liquid waste, however, has recently gained increasing attention as a viable alternative to stream discharge or even to advanced waste treatment (Iskandar et al. 1976). Because a major objective of land treatment is to reduce the concentration of P in wastewater to some acceptable level (perhaps similar to advanced waste treatment), and because plant uptake of P constitutes only a small proportion of the P applied, a knowledge of the soil properties that facilitate P removal is required. These factors should be considered in the selection of a site for wastewater land application. Some soil, such as that used in the Manteca, California, land application system, has a very limited capacity to remove P from municipal wastewater (Iskandar and Syers 1980) and should have not been selected for such purpose. Soils vary considerably in this ability to sorb added P, depending on the amounts and nature of soil components, soil pH, temperature, water content, amounts and forms of P in the applied effluent, and management practices (Monke et al. 1974, Barrow and Shaw 1975, Tofflemire and Chen 1976, Tofflemire et al. 1978, Syers and Iskandar 1981); so there is a need for a method to characterize the soils selected for land application.

Mathematical models can provide potentially useful information on site selection and the prediction of site longevity, as well as on methods for improving the management of land application systems. Several models have been developed with a view toward describing P movement in soils. These range in complexity and scope from rather simple, empirical models which may (Enfield 1974, Ryden and Pratt 1980) or may not (Taylor and Kunishi 1974, Harter and Foster 1976) involve kinetics, to models based on sorption theory and kinetics (Enfield and Bledsoe 1975, Enfield and Shew 1975, Novak et al. 1975, Shah et al. 1975, Enfield et al. 1976, Mansell et al. 1977a, Selim 1978). In some cases, more complex, mechanistic multiphase models have been adopted in which the importance of kinetics is emphasized (Mansell et al. 1977b) or deemphasized (Enfield et al. 1977). Some of these models (Enfield 1974, Enfield et al. 1976) are not concerned with P movement, per se, but with the kinetics of P sorption by soils, which is an important aspect of P movement. Enfield (1978) has reviewed several aspects of empirical sorption theory and mechanistic multiphase models for P movement in soils.

One of the simplest models proposed to date is that of Harter and Foster (1976). It uses an empirical polynomial sorption equation which expresses the relationship between the amount of P sorbed and that added. It takes the form:

$$Y = A + BX + CX^2 + DX^3 + EX^4 \quad (1)$$

where Y = amount of P sorbed
 X = amount of P added .

To obtain this equation, Harter and Foster (1976) added increments of P to the same soil sample in the laboratory. As suggested by Ryden and Pratt (1980), however, several individual but different additions

of P may also be satisfactory. Harter and Foster found that polynomial equations gave a better description of P sorption isotherms than the Freundlich equation. Phosphate breakthrough curves were then calculated by using a simulation model, and estimates of site longevity were obtained. The major advantage of this model is its simplicity in that it avoids the use of "cumbersome" and "inadequate" equations, and does not require a complicated moisture movement computer program for water transport. This approach, however, ignores the kinetics of P sorption that have a varying effect, depending on the soil in question (Ryden et al. 1977b). The importance of including kinetics in empirical models has been emphasized by Enfield (1976), Enfield and Shew (1975), and Enfield et al. (1976). Furthermore, the Harter and Foster model was developed using only one concentration of added P and, without the adoption of a generalized theory of P sorption by soils, the model requires a considerable amount of laboratory work to determine the parameters describing P sorption. In addition, there has been no evaluation of the effectiveness of the model. Nevertheless, this and similar empirical models have potential for predicting P movement in soil and require field evaluation.

The mechanistic multiphase model developed by Mansell et al. (1977b) attempted to describe a much more complex system. Chemical kinetics and transport theory were used to describe the interaction and movement of P in soil. Four phases of soil P were assumed. These were physically absorbed and chemisorbed P as defined by Enfield et al. (1977b) and water-soluble and precipitated phases. The kinetics of reactions between any two of the four phases are considered to be reversible and six kinetic reactions were considered. This model almost certainly represents the first multiphase, kinetic attempt to simulate P movement. The model was used by Mansell et al. (1977b) to describe the transport of applied P during steady water flow assuming a range of rate coefficients. The equations used were as follows:

$$\frac{M(\theta A)}{\partial t} = -\theta (k_1 A^N + k_5 A) + \rho(k_2 B + k_6 D) \quad (2)$$

$$\frac{\partial(\rho B)}{\partial t} = k_1 \theta A^N - (k_2 + k_3) \rho B + k_4 \rho C \quad (3)$$

$$\frac{\partial(\rho C)}{\partial t} = k_3 \rho B - k_4 \rho C \quad (4)$$

$$\frac{\partial(\rho D)}{\partial t} = k_5 (\theta A) - k_6 \rho D \quad (5)$$

where θ = volumetric soil water content
 ρ = soil bulk density
 t = time
 A = concentration of P in solution
 B = amount of P absorbed
 C = amount of P immobilized (chemisorbed)
 D = amount of P precipitated
 N = constant indicating order of the adsorption process
 k_1 = rate coefficient for adsorption
 k_2 = rate coefficient for desorption
 k_3 = rate coefficient for immobilization
 k_4 = rate coefficient for mobilization
 k_5 = rate coefficient for precipitation
 k_6 = rate coefficient for dissolution.

If sorption is considered to be a two-step process, involving a more physical sorption and chemisorption (Ryden et al. 1976), the model could represent a three-phase system, as suggested by Enfield (1978). If chemisorbed P represents the endpoint of the interaction between P and soil components, and precipitation is discounted, the model could be simplified to a two-phase system, but still involve two steps for sorption. As it stands, the model, although versatile, is complex and requires an accurate description of water transport, and this is not always available. Combined multiple mechanistic and transport models may have a greater validity and may be more satisfactory in providing a theoretical description of P movement in soils, but have yet to receive adequate field testing and evaluation.

The complexity of multiple mechanistic and transport models, however, may pose limitations from a practical standpoint in that they require the evaluation of numerous parameters relating to P sorption by the soil at the treatment site, as well as the measurement of a range of field variables. Consequently, there is a need for a generally applicable and simple model to predict P movement in soils that can be applied to existing treatment areas or areas under consideration for use in land treatment that have not been, or are unlikely to be, intensively monitored. The objective of the present study was to evaluate a simple model that was developed with these more practical limitations in mind.

THE P MODEL

General concepts

The concept of the model to be evaluated in the present study has been discussed in detail by Ryden

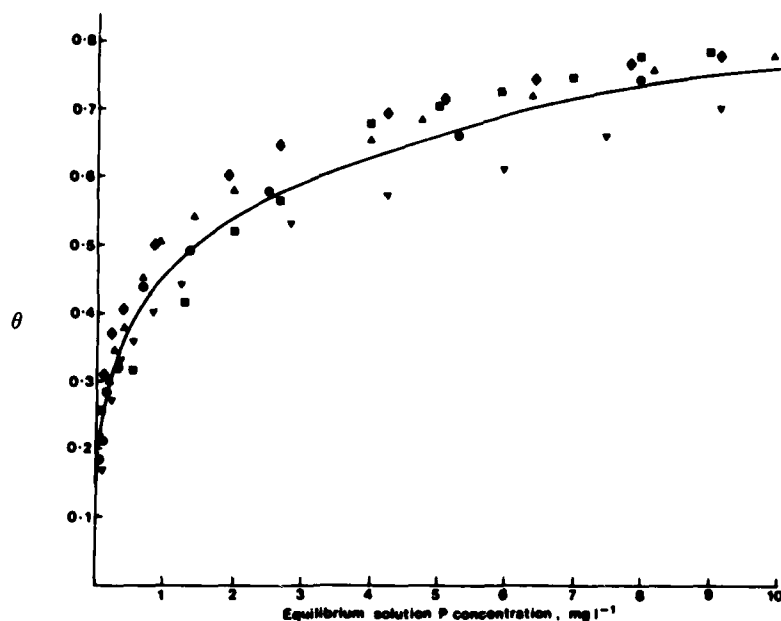


Figure 1. Generalized equilibrium isotherm for P sorption by contrasting soils, where θ (the fractional saturation of the equilibrium sorption maximum) is plotted against the equilibrium solution P concentration. The data points indicated are taken from Ryden et al. (1976) and Ryden and Pratt (1980). The solid line delineating the isotherm is that described by eq 8. (●) Ramona soil; (■) Waikakahi soil; (▲) Egmont soil; (▼) Porirua soil; and (◆) Okaihau soil.

and Pratt (1980). The model relies on the conformity of P sorption by soil at the treatment area to a generalized isotherm (Fig. 1) describing P sorption by soils (Ryden and Syers 1977a). Conformity of P sorption to this generalized isotherm has been observed for a wide range of contrasting subsoils and topsoils (Ryden et al. 1976, Ryden and Syers 1977a, Ryden and Pratt 1980). The generalized isotherm describes the relationship between the fractional saturation (θ) of the maximum P sorption ability of the soil and the solution P concentration at equilibrium. This isotherm provides a simple method of assessing equilibrium sorption capacity at a specified solution P concentration. The specified solution P concentration may be as high as that in the wastewater applied or as low as that regarded as being a maximum by a regulatory agency. Thus the intention of the model is to calculate the capacity of a soil to sorb P at any given equilibrium solution P concentration.

From this estimate of P sorption capacity at the specified solution P concentration (in most cases, the mean dissolved inorganic P concentration of the applied effluent), the longevity of the treatment area may be calculated from eq 6

$$T = \frac{S_p}{I_p - H_p} \quad (6)$$

where T is the time in years for the P front to reach a given depth in the profile, S_p is the P storage capacity in kg ha^{-1} of the volume of soil above that depth for the specified solution P concentration, I_p is the P input in $\text{kg ha}^{-1} \text{ yr}^{-1}$ and H_p is the amount of P removed in any harvested crop.

Equation 6 assumes that the net P input ($I_p - H_p$) reacts progressively with successive depth elements of the soil profile. The sorption capacity, as defined above, of the first depth element becomes saturated before appreciable movement of P into the next depth element. By implication, therefore, the boundary between P-enriched and nonenriched soil is assumed to be rather abrupt. The model also considers that water movement is unimportant relative to the kinetics of the P reactions and that there is sufficient time for slow reactions to have an appreciable impact on the extent of P retention within the soil profile.

Procedures for obtaining model parameters

Values for the parameters in eq 6 are relatively easy to obtain. The values of I_p and H_p can be

determined with reasonable accuracy by well established techniques. The value of S_p is estimated from the generalized P sorption isotherm (Fig. 1), as described below.

The procedures developed for use in the present study involve the determination of the amount of P sorbed at equilibrium for additions of P, resulting in equilibrium P concentrations of between 1 and 10 mg P L⁻¹. The amounts of P to be added should be no more than 600, 1500, and 3000 µg P g⁻¹ soil for soils with expected "low," "medium," and "high" P sorption capacity, respectively. A qualitative estimate of sorption capacity can be made from available information on the mineralogical composition of the soil, and to some extent from soil color, which for B horizon material should provide an indication of the amount of hydrous iron oxides. The laboratory studies to determine the value of S_p must also use soils that have received no wastewater. These can be collected from an area prior to wastewater treatment or from zones contiguous with an existing treatment area. From the determinations of equilibrium P sorption, conformity to the generalized isotherm can be assessed, and the P sorption capacity at a specified solution P concentration can be calculated. The precise procedure is described below.

Samples (4 g) of air-dried, <2-mm soil are shaken with 400 mL of 10⁻² M CaCl₂ containing 40 mg L⁻¹ HgCl₂ and three to five different levels of added P as KH₂PO₄. Shake the bottles on an end-over-end shaker for approximately 72 hr. Remove the bottles and allow to settle for about 2 hr or until the supernatant solution is clear. Remove a 4-mL aliquot of the clear supernatant from the upper 2 cm for the determination of inorganic P (Murphy and Riley 1962). Recap the bottles, continue shaking, and repeat the sampling procedure at approximately 98, 120, 144, 168 and 240 hr using the procedure described above. Solution P concentration at each time interval is plotted against the reciprocal of time, and what should be a linear relationship is extrapolated to infinite time, $t = \infty, 1/t = 0$ (Ryden and Syers 1975). The solution P concentration at $t = \infty$ is taken as the equilibrium value. From this value and the values for the amount of P added and the soil-to-solution ratio, the corresponding value for "equilibrium sorbed P" is calculated.

The amount of native sorbed P present in the soil before P addition must be added to the value of equilibrium sorbed P to give an estimate of total equilibrium sorbed P (x_e) (Ryden et al. 1977b). The amount of native sorbed P is determined by shaking the air-dried, <2-mm soil (2 g) with 30 mL of 0.1 M NaOH for 20 hr. The suspension is centrifuged and the supernatant decanted off. Any soluble organic material in solution is removed using P-free activated charcoal. A suitable aliquot is neutralized, and dissolved inorganic P is de-

termined. The amount of P extracted is expressed per unit weight of soil.

The equilibrium sorption maximum (b_e) may then be calculated (eq 7) from x_e and by reference to the generalized isotherm to obtain the value of θ for the observed equilibrium solution P concentration

$$b_e = x_e / \theta \quad (7)$$

where θ is the fractional saturation of the sorption maximum for the experimentally determined equilibrium solution P concentration. The value of θ can be most accurately determined from eq 8 which describes the generalized isotherm (Fig. 1) over the solution P concentration (c) range of 0 to 12 mg L⁻¹.

$$\theta = 0.778 - (0.455e^{-0.348c}) - (0.217e^{-7.56c}) \quad (8)$$

Conformity of P sorption by the soil under evaluation to the generalized sorption isotherm can be verified by comparison of the b_e values calculated from eq 7 for the different values of x_e obtained during the sorption study. Conformity to the generalized isotherm is verified by essentially constant b_e values.

When conformity to the generalized isotherm has been demonstrated for one depth element within the soil profile, it is reasonable to assume that the remaining depth elements will also conform to this sorption model. Subsequent determinations of b_e for other depth elements will therefore require only one level of P addition. This assumption, however, must not be applied if the soil profile under consideration shows a discontinuity in its mineralogical composition.

The value of x_e corresponding to the specified solution P concentration for each depth element may then be determined from eq 7 using the estimate of b_e , obtained experimentally as described above, and the value of θ calculated from eq 8 for the specified solution P concentration. The value x_e minus the amount of native sorbed P may then be set as S_p when the extent of P sorption is expressed on a weight/volume basis, which requires knowledge of the bulk density of the soil under investigation.

EVALUATION OF THE MODEL

The submodel describing P sorption has been tested for a wide variety of soils with various objectives in view (Ryden et al. 1976, Ryden and Syers 1977a, Ryden and Pratt 1980). The use of this submodel within the P-balance model described by eq 6 has not been previously evaluated. An application that attempts to predict storage capacity and site

longevity at two different sites in New England with three different soils is presented below.

Description of study sites

The land treatment sites used for model evaluation in the present study are located at the Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, New Hampshire, and at Fort Devens, Massachusetts. The CRREL facility consists of six outdoor test cells (8.4x8.4 m and 1.5 m deep) containing either Windsor sandy loam or Charlton silt loam soils. Soil horizons are 0 to 15 cm (A), 15 to 45 cm (B), and 45 to 150 cm (C) for both soils. Particle size analysis of these soils has been presented elsewhere (Iskandar et al. 1979). Wastewater applied to the test cells containing Windsor and Charlton soils had received preapplication treatment to produce either primary or secondary effluents followed by on-line disinfection with ozone or chlorine. Wastewater application commenced in the spring of 1973 and was applied by spray irrigation in varying quantities during the growing season. During the winter of 1974/1975, wastewater was also applied by inundation. A mixture of forage grass was planted in 1973; however, quackgrass (*Agropyron repens* L.) was the predominant species during 1974 and 1975. Forages were harvested three to four times each year. Amounts of P applied, effluent P concentration and plant uptake of P between 1973 and 1978 are discussed later (see Table 3).

For model evaluation, samples of the soil solution were removed using suction lysimeters installed in one test cell for each soil at mean depths of 9.8, 40 and 75 cm. Soil samples were also collected from each test cell during 1979 and the amount of sorbed P was determined by extraction with 0.1 M NaOH as described above.

The Fort Devens site is a rapid infiltration treatment facility which has been in operation since 1946 serving a U.S. military installation. The system consists of 22 treatment beds. In 1973, the flow rate ranged from 2676 to 9541 m³ day⁻¹ (1.3 mgd). Every 14 days, 15 to 20 cm of primary-treated, undisinfected wastewater is applied to each infiltration basin. The wastewater infiltrates within 2 to 3 days. During the summer, vegetation consists of weedy grasses which include (Satterwhite et al. 1976) fall panicum (*panicum dicotomilflorum* Michx.) and barnyard grass (*Echinochloa crusgalli* (L.) Beauv). The soil at this treatment site is a gravelly sand with interspersed lenses of silty sand and sandy gravels. Particle size analysis indicated that only 1 to 3% of the particles are <0.054 mm, 40% are gravel and the rest sand (Satterwhite et al. 1976). The amounts of P applied and effluent P concentration are discussed

later (Table 3). Soil samples were collected from the treatment site during 1979. The amounts of sorbed P were determined by extraction of P with 0.1 M NaOH for several depth elements within the profile, down to approximately 1.6 m.

Conformity of P sorption to generalized isotherm

The time dependence of P sorption by surface horizons of the Windsor, Charlton, and Fort Devens control soils during periods in excess of 72 hr is illustrated in Figure 2. For each soil and P addition, an essentially linear relationship was obtained which was extrapolated to infinite time ($1/t = 0$) to provide an estimate of the equilibrium solution P concentration. The equilibrium solution P concentration varied widely between soils and with the level of P addition, but were all within the desired range of approximately 1 to 10 mg L⁻¹.

The equilibrium solution P concentration obtained for each of four P additions to the surface horizons of each soil are given in Table 1. The values for equilibrium P sorption were calculated from the equilibrium solution P concentration, the level of P addition, and the amount of native sorbed P present in each control soil. The values obtained are those for x_e in eq 7. The values of θ for each equilibrium solution P concentration were calculated from eq 8 describing the generalized P sorption isotherm (Fig. 1) and the corresponding b_e values obtained from eq 7 are given in Table 1.

Despite the wide range in P addition to each soil, the values for b_e were essentially constant for a particular soil. The coefficients of variation associated with the mean value of b_e for each soil ranged from only ± 2.9 to 8.5%. These findings are consistent with those for a Ramona sandy loam from California (Ryden and Pratt 1980). The consistency of b_e values for a particular soil (Table 1) clearly indicates that P sorption by each soil conformed to the generalized isotherm for P sorption by soils (Fig. 1). It is reasonable to assume, therefore, that the isotherm can be used in the prediction of S_p for these and other depth elements of the soil profiles used in the present study.

Estimates of b_e for additional depth elements of the Windsor, Charlton, and Fort Devens profiles are given in Table 2. These estimates were based on the determination of an x_e value from a single addition of P to each soil. Each P addition resulted in an essentially linear relationship between solution P concentration and the reciprocal of time. The values of b_e for each depth element suggest appreciable variation in equilibrium P sorption within each profile, with highest values generally being observed in the upper part of the profile. In the case of the

Table 1. Data for equilibrium sorption of P by the surface horizons of Windsor, Charlton, and Fort Devens soils derived from the kinetics of P sorption and the generalized P sorption isotherm for soils.

Added P ($\mu\text{g g}^{-1}$)	Equilibrium P concentration* (mg L^{-1})	Equilibrium P sorption† ($\mu\text{g g}^{-1}$)	θ^{**}	Equilibrium sorption maximum (b_e) ($\mu\text{g g}^{-1}$)
Windsor sandy loam				
625	2.10	708	0.559	1270
875	3.45	823	0.641	1280
1250	6.12	931	0.723	1290
1750	9.80	1060	0.763	1390
				1310 \pm 60
Charlton silt loam				
625	1.80	720	0.535	1350
875	2.90	860	0.612	1410
1250	5.55	975	0.712	1370
1750	9.35	1090	0.760	1430
				1390 \pm 40
Fort Devens gravelly sand				
250	0.75	268	0.427	628
750	4.20	423	0.670	631
1125	6.85	533	0.736	724
1500	10.3	563	0.765	735
				680 \pm 58

* Estimated from Figure 2.

† Includes native sorbed P (293, 275 and 93 $\mu\text{g P g}^{-1}$ for Windsor, Charlton and Fort Devens, respectively).

** Calculated from eq 8 describing the generalized P sorption isotherm (Fig. 1).

Table 2. Estimation of b_e values for the additional horizons of the Windsor, Charlton, and Fort Devens soils.

Soil	P added ($\mu\text{g g}^{-1}$)	Equilibrium solution P concentration (mg L^{-1})	P sorbed ($\mu\text{g g}^{-1}$)	Native sorbed P ($\mu\text{g g}^{-1}$)	x_e ($\mu\text{g g}^{-1}$)	θ	b_e ($\mu\text{g g}^{-1}$)
Windsor B	1000	4.15	585	223	808	0.670	1200
Windsor C	500	2.15	285	124	409	0.563	726
Charlton B	2000	2.00	1800	142	1940	0.551	3520
Charlton C	1000	3.45	655	206	861	0.641	1340
Fort Devens (6-25 cm)	750	2.05	495	123	618	0.555	1110
Fort Devens (50-75 cm)	750	4.35	315	52	367	0.678	541
Fort Devens (102-163 cm)	750	4.85	265	54	319	0.693	460

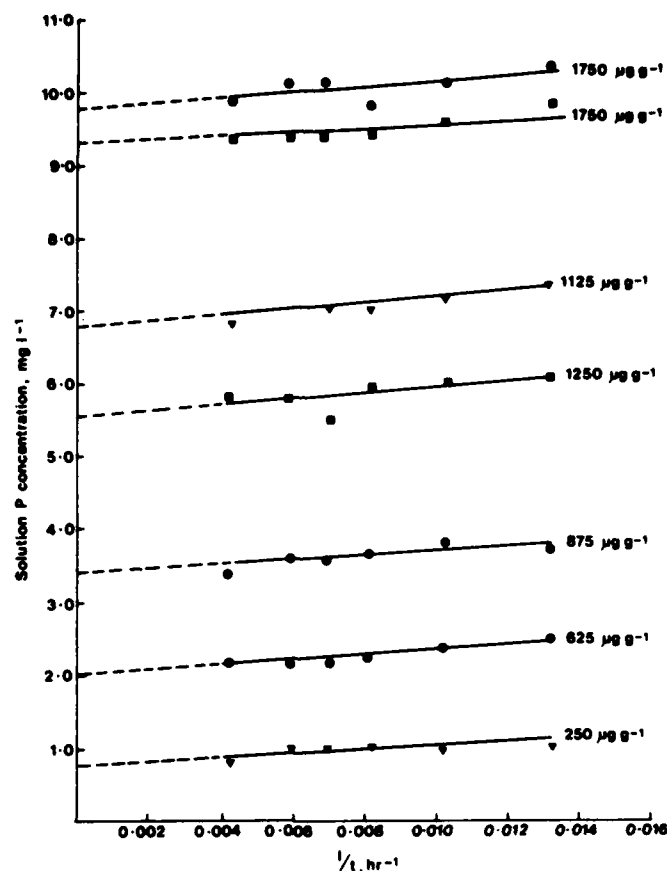


Figure 2. Relationships between solution P concentration and reciprocal of time for various additions of P (indicated against each relationship) to soil from the surface horizons of Windsor sandy loam (●), Charlton silt loam (■), and Fort Devens gravelly sand (▼). Extrapolation (dashed line) to infinite time ($1/t = 0$) gives an estimate of equilibrium solution P concentration.

Charlton and Fort Devens soils, the second depth element has an appreciably higher P sorption capacity than any of the other depth elements.

Determination of S_p and site longevity

As indicated previously, the value of S_p (eq 6) may be determined from b_e and the value of θ for a specified solution P concentration. In the present evaluation, the specified solution P concentration was set as that in the effluent being applied to the soil profile. These values are given in Table 3. Hence, the storage capacity of the profile is assumed to be limited by the x_e value corresponding to the average solution P concentration in the effluent.

The values of the parameters involved in the determination of S_p for each depth element in each

profile are given in Table 3 in the sequence in which they are required in the calculation. In the case of Windsor soil, the mean P concentration in the applied effluent is 5.2 mg L^{-1} . This concentration gives a θ value of 0.704 from eq 8 and an x_e value of $921 \text{ } \mu\text{g P g}^{-1}$ for the A horizon. The net sorption capacity (net x_e) at 5.2 mg L^{-1} is $628 \text{ } \mu\text{g P g}^{-1}$ when the amount of native sorbed P is deducted from the value of x_e . Based on a depth element of 15 cm and a bulk density within this element of 1.38 g cm^{-3} , the storage capacity S_p is found to be $1300 \text{ kg P ha}^{-1}$. Similar calculations provided estimates of S_p for the other depth elements of each soil (Table 3).

The total storage capacity of each profile can be determined by summation of the individual S_p values for each depth. The total storage capacity for the

Table 3. Annual input and crop removal of P and data required in the calculation of storage capacity (S_p) for each soil.

Horizon	Depth (cm)	θ for P concentration of effluent ($\mu\text{g g}^{-1}$)	b_e ($\mu\text{g g}^{-1}$)	x_e ($\mu\text{g g}^{-1}$)	Native sorbed P ($\mu\text{g g}^{-1}$)	Net x_e ($\mu\text{g g}^{-1}$)	Bulk density (g cm^{-3})	S_p (kg P/ha)
Windsor sandy loam*								
A	0-15	0.704	1310	921	293	628	1.38	1300
B	15-46	0.704	1210	848	233	626	1.58	2970
C	46-137	0.704	726	511	124	387	1.53	6220
Charlton silt loam†								
A	0-15	0.704	1390	979	275	704	1.08	1140
B	15-46	0.704	3520	2480	142	2340	1.46	10,500
C	46-137	0.704	1330	946	206	740	1.71	13,300
Fort Devens gravelly sand**								
-	0-6	0.764	680	520	93	427	1.4††	169
-	6-25	0.764	1110	851	123	728	1.4	910
-	50-76	0.764	541	413	52	361	1.4	617
-	102-163	0.764	460	351	54	297	1.4	1190

*Average P conc. of effluent = 5.2 mg L^{-1} ; total P input = $243 \text{ kg ha}^{-1} \text{ yr}^{-1}$; P removed in harvested crop = $33 \text{ kg ha}^{-1} \text{ yr}^{-1}$.

†Average P conc. of effluent = 5.2 mg L^{-1} ; total P input = $145 \text{ kg ha}^{-1} \text{ yr}^{-1}$; P removed in harvested crop = $29 \text{ kg ha}^{-1} \text{ yr}^{-1}$.

**Average P conc. of effluent = 10 mg L^{-1} ; P input = $2470 \text{ kg ha}^{-1} \text{ yr}^{-1}$; P removed in harvested crop = $0 \text{ kg ha}^{-1} \text{ yr}^{-1}$.

††Estimated value for $<2 \text{ mm}$ material which is 47% of a given soil volume.

Charlton soil to a depth of 137 cm ($24,700 \text{ kg ha}^{-1}$) greatly exceeded that ($10,500 \text{ kg ha}^{-1}$) for the Windsor soil. This reflects the appreciably higher sorption maxima of the B and C horizons in the Charlton soil.

The longevity of each profile, before appreciable P breakthrough at the maximum depth sampled, can be calculated from eq 6 and the information in Table 3. In the case of the Windsor profile, $S_p = 10,500 \text{ kg ha}^{-1}$ and $(I_p - H_p) = 210 \text{ kg ha}^{-1} \text{ yr}^{-1}$. Assuming the continuance of present management, the front of P enrichment within the profile should not reach 137 cm for approximately 50 years from the inception (1974) of land treatment of wastewater on this soil. The longevity for the Charlton soil to the same depth is 213 years, reflecting the appreciably greater storage capacity of this profile.

Similar calculations for the Fort Devens profile indicate a net storage capacity to 163 cm of 5280 kg ha^{-1} , when it is assumed that S_p values for depth elements that were not sampled are the average of the values for the elements immediately above and below. Hence, the longevity of the Fort Devens profile for a P input of $2470 \text{ kg ha}^{-1} \text{ yr}^{-1}$ is approximately 2 years. As wastewater has been added to this profile since 1946, these calculations suggest

that the storage capacity of the profile to be depth of 163 cm has long been saturated. Field measurements of the P enrichment within the profile at the Fort Devens treatment area are consistent with this prediction, as discussed below.

Prediction of the depth of P enrichment

The accumulation of NaOH-extractable P within the soil profiles receiving wastewater may be used as an index of the depth to which the front of P enrichment has moved. This assumption is reasonable since the major portion of the total P applied is in the form of dissolved inorganic P which will be largely retained in the pool of sorbed P. Mineralization of applied organic P will also ultimately contribute to the pool of sorbed P. It is this pool which is removed during NaOH extraction (Williams et al. 1967, Ryden et al. 1977a).

In the case of the Windsor soil, appreciable enrichment of NaOH-P had occurred to a depth of 15 cm with additional limited enrichment in the 15 to 30 cm depth (Table 4). The total NaOH-P enrichment of the profile was 1260 kg ha^{-1} which compared favorably with the net P input of 1050 kg ha^{-1} between 1974 and 1979. The data in Table 4 suggest

Table 4. Enrichment in NaOH-extractable P in different depth elements of the Windsor, Charlton and Fort Devens profiles after treatment with wastewater, and the corresponding estimates of storage capacity.

<i>NaOH-extractable P (kg ha⁻¹)</i>				
<i>Depth (cm)</i>	<i>Control*</i>	<i>1979</i>	<i>NaOH-P</i>	<i>Storage capacity†</i>
<u>Windsor sandy loam</u>				
0-7.5	303	830	527	650
7.5-15	303	845	542	650
15-30	528	710	182	1480
30-45	528	517	-	1480
45-60	287	298	11	1010
			$\Sigma =$	1260
Net P input =				1050
<u>Charlton silt loam</u>				
0-7.5	222	956	734	570
7.5-15	222	228	-	570
15-30	330	428	98	5120
30-45	330	367	37	5120
			$\Sigma =$	859
Net P input =				580
<u>Fort Devens gravelly sand</u>				
0-6	35	142	107	169
6-25	150	745	605	910
50-76	78	680	602	617
102-163	190	1280	1090	1190

* Soil materials collected prior to wastewater addition.

† S_p value for the solution P concentrations specified in Table 3.

that the front of P enrichment is at about 15 cm, with some spread into the 15- to 30-cm depth. Significantly, however, 85% of the total P enrichment occurred in the 0- to 15-cm depth. If the zone of P enrichment was defined by a sharp boundary, as is assumed in the P budget model described by eq 6, the front of P enrichment would have been predicted to have reached 12 cm, based on the net P input and the storage capacity of the profile. Consequently, the model suggests close agreement between predicted and measured depths of P enrichment in the Windsor soil.

Similarly, the predicted and measured depths of P enrichment were in close agreement for the Charlton soil. Appreciable accumulation of NaOH-extractable P was only observed for the 0 to 7.5 cm profile depth (Table 4) in which 86% of the total P enrichment occurred. Based on the storage capacity of the profile and the net P input, the predicted depth of the front of P enrichment is 7.6 cm, in very close agreement with the field observations.

Table 5. Measured and predicted soil solution P concentrations in different depth elements of the Windsor, Charlton and Fort Devens soils.

Depth (cm)	Dissolved inorganic P in soil solution (mg L ⁻¹)	
	Measured values (mean and range)*	Predicted values†
Windsor sandy loam		
7.5-12	0.245 (0.040-0.441)	3.0
35-45	0.031 (0.001-0.069)	0.055
70-80	0.015 (0.001-0.060)	n.d.**
Charlton silt loam		
7.5-12	0.041 (0.001-0.067)	0.060
35-45	0.019 (0.001-0.052)	0.010
70-80	0.015 (0.001-0.029)	n.d.
Fort Devens gravelly sand		
6-25	8 (5-13)	1.8
50-76	8 (5-11)	6.8
102-163	8 (5-12)	5.1

* On nine days during October and November 1979 (total of 27 samples), except Fort Devens for which values are drawn from Satterwhite et al. (1976).

† Predicted from the existing saturation of the sorption maximum after application of wastewater; details in text.

**Not determined; appropriate information not available.

The depth of P enrichment is also reflected in measured dissolved inorganic P concentrations in the soil solution at various depths in the undisturbed profile (Table 5). In the case of Windsor soil, the soil solution P concentration at a mean depth of 9.8 cm (within the depth of P enrichment) was approximately 10 times greater than that at 40 cm, a depth outside the zone of P enrichment. For Charlton soil, the soil solution P concentration at a mean depth of 9.8 cm was only about twice that observed at lower depths where no P enrichment had occurred. This is consistent with the fact that the predicted and measured depths of P enrichment were at only 7.5 cm in the Charlton soil, and suggests a sharp boundary between the P-enriched and nonenriched zones within the profile.

The P sorption submodel and the values for NaOH-extractable P can also be used to predict the dissolved inorganic P concentrations in the soil solution at a particular depth. This is achieved by setting $\theta = \text{NaOH-P}/b_e$ and calculating the corresponding solution P concentration from eq 8. Where comparisons can be made, predicted solution P concentrations agreed, with one exception, moderately well with the measured values (Table 5).

In the case of Fort Devens soil, NaOH-extractable P showed considerable enrichment for all depth

elements as compared to the control soils (Table 4). The net enrichment of NaOH-P agreed fairly well with the storage capacity of each depth element of this profile, particularly at the greater depths. These data (Table 4) suggest that the Fort Devens profile is saturated, with respect to P sorption from effluent having a mean P concentration of 10 mg L^{-1} . The saturation of the Fort Devens profile was predicted in the calculation of site longevity, and is reflected by the mean and range of soil solution P concentrations measured at various depths in the profile (Table 5). These concentrations are essentially the same as that for the untreated effluent and suggest the lack of further P removal in the upper 163 cm of the profile. As for Windsor and Charlton soils, the soil solution P concentration predicted from the P sorption submodel were of the same order as the measured concentrations.

ADVANTAGES AND LIMITATIONS OF THE MODEL

The objective of the model described and evaluated in the preceding discussion was to predict the storage capacity of a soil profile with respect to P sorption, and thereby to predict site longevity during land treatment of wastewaters. In this respect, the model has been successful in predicting the lower depth of the zone of P enrichment in two soil profiles, Windsor and Charlton, to which wastewater had been applied for 5 years. In the case of the Fort Devens soil, field measurements of P enrichment were in agreement with the prediction that the P storage capacity of this profile had been saturated and that wastewater was passing the 163-cm depth essentially unchanged with respect to P concentrations.

Although the model supplies only one item of information, in many practical situations an estimate of the P storage capacity of a soil profile may be all that is required when evaluating a site for wastewater treatment. The model can be used to evaluate not only proposed treatment areas but also the condition of existing treatment areas, providing that soil materials representative of the treatment area before wastewater application are available. The latter may generally be obtained from land contiguous with the treatment area.

Although the generalized P sorption isotherm can be used to predict solution P concentrations, the P sorption submodel is less successful in the prediction of soil solution P concentration at a particular stage after the initiation of wastewater treatment. This probably reflects the fact that the P sorption sub-

model is based only on considerations of P sorption and does not include the impact of desorption hysteresis (Barrow and Shaw 1975, Ryden and Syers 1977b) in controlling soil solution P concentration.

The model also assumes a sharp boundary between the zone of P enrichment and the nonenriched soil below. Preferential movement of solution P through macropores and channels (Kanchanasut et al. 1978, Thomas and Phillips 1979) within the profile will result in a more rapid movement of solution P to greater depths than predicted by the present model. This limitation is shared with other models in that they all assume uniform movement of water and solute through the profile. Nevertheless, field data (Tables 4 and 5) obtained for low-rate treatment on the Windsor and Charlton soils suggest that the assumption of a sharp boundary may be reasonably valid.

The P sorption submodel used in the present study assumes that sorption is the only process involved in P retention by soils. This assumption is probably valid for a wide range of soil types, as discussed by Syers and Iskandar (1980). However, on calcareous soils and at high solution P concentrations, it is possible that precipitation of calcium phosphates may make a significant contribution to P retention (Holford and Mattingly 1975). In such circumstances, data may not conform to the generalized sorption isotherm. Furthermore, extraction of soils with NaOH does not remove precipitated calcium phosphates, and the model may lead to an underestimation of the P storage capacity.

The present model has several practical advantages, a major one being that the P sorption submodel requires only a small number of laboratory measurements. If it is assumed that P sorption by a particular soil conforms to the generalized P sorption isotherm, the storage capacity of a single depth element can be determined from only two laboratory measurements and an estimate of the bulk density of the undisturbed soil. As an increasing number of soils appear to conform to the generalized P sorption isotherm, it may be possible in future applications of this model to eliminate the procedure for establishing conformity to the generalized isotherm (Table 1). The assessment of P sorption at equilibrium using extrapolation to infinite time eliminates the impact of soil-to-solution ratio on the estimate of P sorption by soils (Hope and Syers 1976). The use of soil suspensions and a wide soil-to-solution ratio provides a simpler method of assessing P sorption by soils than the use of saturated soil pastes, soil cores, or soil columns.

The model developed in the present study offers potential for a simple estimation of the P storage capacity of the soil profile. Initial application of the model has produced encouraging results, but

further evaluation is required on other sites before its general applicability can be established.

CONCLUSIONS

The P model evaluated in the present study adequately predicted site longevity in terms of P removal from applied wastewater. The model has been successful in predicting the lower depth of the zone of P enrichment in two soil profiles, Windsor and Charlton, to which wastewater had been applied for 5 years. In the case of the Fort Devens soil (gravelly sand), field measurements of P enrichment were in agreement with the prediction that the P storage capacity of this profile had been saturated and that wastewater was passing the 163-cm depth with P concentrations essentially unchanged. The P model is particularly useful in selecting and evaluating sites for land treatment, as well as for site management.

RESEARCH NEEDS

As indicated above, the model evaluated in the present study has previously received only limited evaluation. The P sorption submodel requires more extensive evaluation using a wide range of soil types from different localities. The applicability of the submodel will be most easily established by testing equilibrium P sorption data for conformity with the generalized P sorption isotherm. In particular, the P sorption submodel requires further evaluation using calcareous soils to evaluate the possible importance of precipitation in P removal by these soils. The use of the P sorption submodel to predict storage capacity and the P balance model to predict site longevity requires use and evaluation at a wide range of wastewater treatment sites. This evaluation will be most valuable if conducted at treatment sites that have been in operation for at least 5 to 10 years and where soil samples, representative of the profile wastewater addition, are available. Information obtained in these studies will define the scope of applicability of this simple model to determine storage capacity and site longevity with respect to P removal from wastewater.

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